Photochemical Dimerization of Resin Acids

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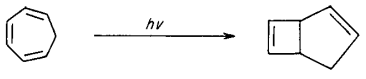
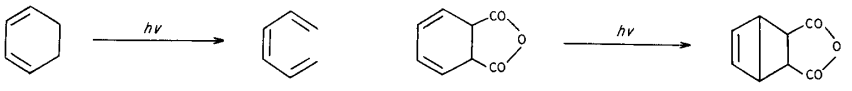
Abstract——Ultraviolet irradiation of levopimaric acid with a sensitizer gave dimer (II), 8, 12-bridged valence tautomer (III) and dehydroabietic acid (VI). The yield of the dimer (III) increased with increasing amount of the sensitizer. Ultraviolet irradiation of abietic acid (IV) either with or without the sensitizer gave dimer (V), although the reaction with the sensitizer was more rapid. The dimer (II) of levopimaric acid was thermally stable and had a high melting point (above 300°C), while the dimer (V) of abietic acid was thermally unstable and regenerated abietic acid when heated at 70°C.

Introduction

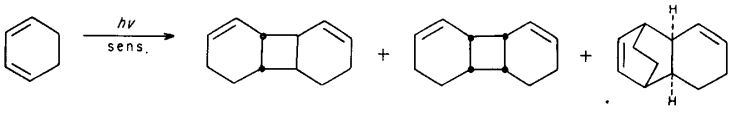
Conjugated cyclic dienes upon ultraviolet irradiation have been found to undergo two modes of reactions, bond formation and bond cleavage. Irradiation of 1, 3-cycloheptadiene systems effects valence isomerization to bicyclo[3.2.0]heptene systems and the numerous cycloheptadienes have been transformed to attest the generality of the process[1~3].



The photoreaction of 1, 3-cyclohexadiene may be either the ring-formation reaction of the ring-cleavage reaction. The ring-cleavage reaction occurs from the irradiation of the parent compound, while the ring-formation reaction occurs from the irradiation of the derivative as follows[4,5].



Also photosensitized dimerizations have been reported for cyclohexadiene and related systems[6,7].



Photochemical transformation of the diene systems in the steroids such as the ring-

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closure, ring-opening, and dimerization have been extensively studied[8~11]. However reports on the diterpene resin acids are few, and photolytic valence isomerizations of levopimaric acid and palustric acid have been reported[11,12]. No photodimerization of resin acids has been reported although their dimerization in photoreaction is expected. The purpose of the present work is to investigate the photodimerization of conjugated diene systems in resin acids.

Experimental

The nmr spectrum was recorded on a Hitachi R-22 spectrometer, TMS being used as an internal standard. The mass spectrometry was conducted by using a Shimazu-LKB 9000 gas chromatograph-mass spectrometer. The uv spectrum was measured by using a Hitachi-124 spectrophotometer. The IR spectrum and optical rotation were measured by using a JASCO IR-S spectrophotometer and a JASCO-DIP-SL automatic polarimeter, respectively.

Preparation of starting and reference substances

Levopimaric acid was prepared from fresh pine oleoresin by a modification[13] of the amine salt technique of HARRIS[14]; $[\alpha]_D$ −270°; mp 150~151°C; λ_{max}^{EtOH} nm (ε): 272 (7100). Abietic acid was isolated from commerical rosin with the amine salt technique of HARRIS[14]; $[\alpha]_D$ −110°; mp 170~171°C; λ_{max}^{EtOH} 241 (23000). Dehydroabietic acid was isolated from the commercial disproportionated rosin by the amine salt method with 2-amino-2-methyl-1-propanol; $[\varepsilon]_D$ +63°; mp 171~172°C. Palustric acid was prepared from pine gum by the method of Joye et al.[15]; $[\alpha]_D$ +70°; mp 162~166°C; λ_{max}^{EtOH} nm (ε): 265 (8600). Methyl esters of levopimaric acid, abietic acid, dehydroabietic acid, and palustric acid were prepared by esterification of the acids with diazomethane in ether. 8, 12-bridged valence tautomer (III) was prepared by the nonsensitized photoirradiation of levopimaric acid under nitrogen[11].

Irradiation of levopimaric acid (I) with a sensitizer

Levopimaric acid (I) (500 mg) and acetophenone (50 mg) were dissolved in n-hexane (25 ml) in a pyrex flask and the air in the flask was replaced by nitrogen. The flask cooled by running water was irradiated with a 450W high pressure mercury lam. Samples were removed at intervals, stripped under reduced pressure (bath temperature, below 30°C), treated with diazomethane in ether and developed on silica gel plate containing 5% $AgNO_2$ with cyclohexane-ether (20 : 1). A precipitate occured during the photoreaction. After irradiation for 15 hr, the precipitate (50 mg) was separated from the solution by filtation. The filtrate was evapolated under reduced pressure. The residue was treated with etheral diazomethane and submitted to preparative thin layer chromatography on Merk Silica gel PF_{254} containing 5% $AgNO_3$ with cyclo-

hexane-ether (20 : 1). Products were eluted with ether from the silica gel. Methyl dehydroabietate (VI) and the methyl ester of isomer (III) were obtained in a yield 6 and 70 % respectively. The yield of the precipitate was increased with increasing amount of acetophenone (10 % with 50 mg, 16 % with 100 mg, 20 % with 200 mg of acetophenone). The precipitate was sparingly soluble in ether, methanol, acetone, chloroform and dioxane but readily soluble in pyridine. The precipitate was washed with ether ane esterified with diazomethane. The methyl ester of the precipitate was shown to be the methyl ester of dimer (II) by means of its nmr, IR, mass, and uv spectra. When benzophenone was used as the sensitizer instead of acetophenone, the photoreaction of levopimaric acid gave also the dimer (II), isomer (III), and dehydroabietic acid (VI).

Irradiation of levopimaric acid (I) without a sensitzer

A solution of levopimaric acid (500 mg) in n-hexane (25 ml) was irradiated with a high pressure mercure lamp under nitrogen for 15 hr and only the 8, 12-bridged valence tautomor (III) was obtained by the same procedure as mentioned above. The precipitate did not occur.

Methyl ester of dimer (II)

The methyl ester of dimer (II) is corloress crystals; mp 198°C; $[\alpha]_D$ +170°; λ_{max}^{EtOH} nm (ε) : 220 (14500); MS m/e : 632 (M^+); IR ν_{max}^{KBr} cm^{-1} : 1740 ($C_{18}=O$); NMR δ : 5.40 (1H, s, C-14 proton), 3.64 (3H, s, methoxyl group), 2.30 (2H, m, C-15, C-12 allylic protons), 1.22 (3H, s, C-19 methyl protons), 0.78 (3H, s, C-20 methyl protons), 0.80 (3H, d, J=7Hz, methyl protons of isopropyl group), 0.62 ppm (3H, d, J=7Hz, methyl protons of isopropyl group). Anal. Calcd. for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19. Found: C, 79.15; H, 10.33.

Methyl ester of isomer (III)

The methyl ester of isomer (III) did not crystallize; MS m/e : 316 (M^+); NMR δ : 5.76 (1H, q, C-14 vinyl proton), 3.63 (3H, s, methoxyl protons), 1.26 (3H, s, C-19 methyl protons), 1.07 (3H, s, C-20 methyl protons), 1.03 (3H, d, J=7Hz, methyl protons of isopropyl group), 1.00 ppm (3H, d, J=7Hz, methyl protons of isopropyl group). The nmr and mass spectra of the methyl ester of the compound (III) were identical with those of the methyl ester of an authentic isomer (III) prepared by nonsensitized photoisomerization method of LAWRENCE et al.[11]

Methyl dehydroabietate from levopimaric acid

The methyl ester of compound (VI) was recrystallized with methanol-water. The nmr and spectra of the methyl ester of compound (VI) were identical with those of the authentic methyl dehydroabietate.

Irradiation of abietic acid (IV) without a sensitizer

5 g of abietic acid (V) was dissolved in 250 ml of n-hexane in a pyrex flask. The air in the pyrex flask was completely replaced by nitrogen. The flask cooled by running water was irradiated with a 450W high pressure mercury lamp. The reaction was followed by the change in specific rotation and also by frequent determinations of absorption spectrum from 220~320 nm. After 96 hr, the solvent was removed *in vacuo* at 30°C. The TLC (5% $AgNO_3$, cyclohexane : ether = 20 : 1) and nmr spectrum of the methyl esters of the reaction products showed that the methyl ester was composed almost of the methyl ester of compound (V).

Irradiation of abietic acid with a sensitizer

A solution of 5 g of abietic acid and 500 mg of benzophenone was irradiated with a high pressure mercury lamp for 60 hr under nitrogen, and 3 g of compound (V) was obtained by the same procedure as mentioned above. The rate of the photodimerization increasing amount of the sensitizer.

Dimer (V) of abietic acid

Compound (V) was recrystallized from n-hexane in fine prisms ; $[\alpha]_D$ +169° ; λ_{max}^{EtOH} nm (ε) : 223 (13900) ; MW 604 (Calculated from the MW of the methyl ester which was measured by cryoscopic method and the mass spectrum of the methyl ester, MS m/e : 316) ; NMR δ : 5.47 (1H, s, C-14 proton), 2.20 (2H, m, C-7 and C-9 allylic protons), 1.17 (3H, s, C-19 methyl protons), 0.82 (3H, s, C-20 methyl protons), 0.95 ppm (6H, d, J=7Hz, methyl protons of isopropyl group) ; IR ν_{max}^{KBr} cm^{-1} : 1740 (C_{18}=O). Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.42 ; H, 10.00. Found : C, 79.48 ; H, 10.52.

Irradiation of palustric acid with acetophenone

500 mg of palustric acid and 250 mg of acetophenone were dissolved in 25 ml of n-hexane in a pyrex flask. The air in the flask was completely replaced by nitrogen. The flask cooled by running water was irradiated with a 450W high pressure mercury lamp. The aliquots were taken at intervals for measurement of the optical rotation. After 50 hr, the solvent was removed under reduced pressure. The residue was dissolved in 5 ml of acetone and 300 mg of 2-amino-2-methyl-1-propanol was added. The suspension was cooled, and the salt was filtered. The amine salt was suspended in ether and shaken vigorously with 2N-CH_3COOH until the amine salt crystals disappeared. The ether solution was washed with water and then the ether was removed under reduced prossure. The nmr spectrum of the residue showed that the residue was composed almost of dehydroabietic acid (VI).

Irradiation of palustric acid without a sensitizer

500 mg of palustric acid was dissolved in 25 ml of n-hexane in a pyrex flask. The air in the flask was completely replaced by nitrogen. The flask cooled by running water was irradiated with a 450W high pressure mercury lamp. The photoreaction

was followed by the change in specific rotation and also by frequent determinations of absorption spectrum from 220~320 nm. After 40 hr, the specific rotation became constant, and then the solvent was removed under reduced pressure. The nmr of the residue exhibited the signals corresponding to five vinyl protons of the ring-opened triene (VIII) at δ 4.76 (a complex pattern) and 5.75[12], a vinyl proton of palustric acid at δ 5.37. The high-field multiplet at δ 4.76 had an area four times the area of the low field of absorption at δ 5.75. The area ratio of the bands at δ 5.75 and 5.37 was 1/4.

The thermal treatment of dimer (V)

A solution of 50 mg of dimer (V) in 100 ml of methanol was kept at 70°C for one hour. The reaction was followed by the change in specific rotation and by frequent determinations of absorption spectrum from 220~230 nm. After one hour, the specific rotation and the uv spectrum of the solution were identical with those of abietic acid. The solvent was removed *in vacuo* and the products were treated with etheral diazomethane. The nmr spectrum of the methyl ester showed that the methyl ester was composed of only methyl abietate. The total area of the vinyl region when compared to the area of methoxyl group signal indicated an average of to vinyl protons.

Results and Discussion

A solution of levopimaric acid (I) and a sensitizer (acetophenone or benzophenone) in n-hexand under nitrogen was irradiated with a high pressure mercury lamp. A hexane-insoluble precipitate occured during the photoreaction. The yield of the precipi-

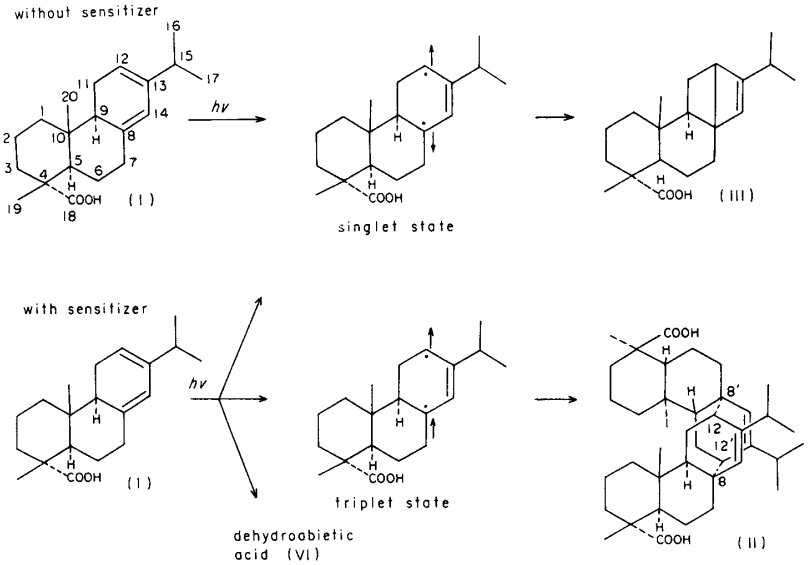

Fig. 1.

tate (II) increased with increasing amount of the sensitizer (10 % with 50 mg, 16 % with 100 mg, 20 % with 200 mg of acetophenone). The melting point of the precipitate was higher than 300°C and the melting point of the methyl ester was 198°C. Dehydroabietic acid (VI) and 8, 12-bridged valence tautomer (III) were obtained from the hexan-soluble portion. The yield of dehydroabietic acid also increased with increasing amount of the sensitizer. Without a sensitizer only the 8, 12-bridged valence tautomer was obtained in the irradiation of levopimaric acid (I). Their structure were elucidated as follows.

Since the precipitate was sparingly soluble in organic solvents, methanol, ether, etc., the purification was conducted by esterification with diazomethane. The elemental analysis and mass spectrum of the seter of compound (II) indicated the formula $(C_{21}H_{32}O_2)_2$. The IR spectrum of the compound showed no hydroxyl group and no carbonyl function except C-18 carbonyl function. The uv spectrum showed the characteristic absorption maximum at 220 nm ($\varepsilon=14500$). The nmr spectrum of the ester exhlbited absorption corresponding to a vinyl proton at δ 5.40 (1H, s), a methoxyl group at δ 3.64 (3H, s), two allylic protons at δ 2.30 (2H, m), methyl groups at δ 0.78 (3H, s), 1.22 (3H, s), 0.80 (3H, d, J=7Hz) and 0.62 ppm (3H, d, J=7Hz). On the basis of the above data, we propose the structure of II for the pecipitate. An unusual absorption at 220 nm in photoproduct (II) must in some manner own its low energy to the proximity of the π orbitals of the double bonds by forming C_{12}–$C_{8'}$ bond and C_8–$C_{12'}$ bond[16,17]. The proximity of the π orbitals of the double bonds can not be sterically expected provided C_{12}–$C_{12'}$ and C_8–$C_{8'}$ bonds are formed in the dimer. Since the C-20 methyl group is in close contact with the C-11 methylene group provided C_{12}–$C_{8'}$ and C_8–$C_{12'}$ bonds are formed in the β-side, C_{12}–$C_{8'}$ and C_8–$C_{12'}$ bonds seem to be formed on the α-side in the dimer.

The methyl esters of compound (III) and (VI) were identical with those of the methyl esters of authentic samples prepared with nonsensitized photoisomerization method of LAWRENCE et al.[11] and with the amine salt technique.

Abietic acid (IV) in n-hexane was irradiated under nitrogen with a high pressure mercury lamp. After 96 hr, the TLC of the solution showed almost the spot of com-

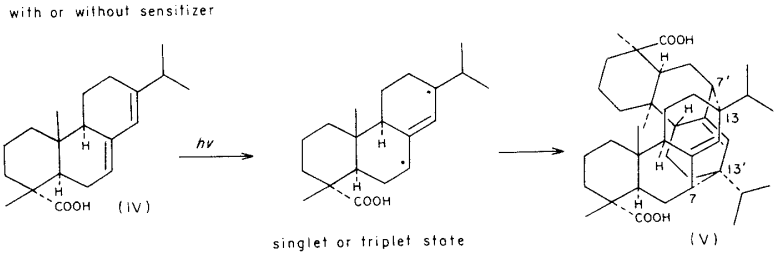

Fig. 2.

pound (V). Either with or without a sensitizer, irradiation of abietic acid gave same photoproduct (V), although the reaction with a sensitizer was faster. Photoproduct (V) was thermally unstable, and abietic acid was regenerated when heated for one hour at 70°C. The structure of the compound (V) was elucidated as follows.

The elemental analysis, mass spectrum and the molecular weight of the methyl ester by cryoscopic method exhibited the formula $(C_{21}H_{32}O_2)_2$. The IR spectrum of the methyl ester of compound (VI) exhibited no hydroxyl group and no carbonyl function except C-18 carbonyl function. The uv spectrum of the compound (V) showed a characteristic absorption maximum at 223 nm ($\varepsilon=13900$). The specific rotation of the compound (V) was +169°. The nmr spectrum of the compound (V) exhibited absorption corresponding to a vinyl proton at δ 5.47 (1H, s), two allylic protons at δ 2.20 (2H, m) methyl groups at δ 1.17 (3H, s), 0.82 (3H, s), 0.95 (6H, d, J=7Hz). Above data enabled us to propose the structure of V for the compound. On bath cases of C_7–$C_{7'}$, C_{13}–$C_{13'}$, bonds and C_{13}–$C_{7'}$, C_7–$C_{13'}$ bonds in the dimer (V), the proximity of the π orbitals of the double bonds can be sterically expected, but comparative large value in the specific rotation may be due to rotation to the same direction in each unit of the dimer by forming C_7–$C_{13'}$ and C_{13}–$C_{7'}$ bonds. Each unit of the dimer (V) seems to rotate opposite direction and then $[\alpha]_D$ may be small or zero provided C_7–$C_{7'}$, and C_{13}–$C_{13'}$ bounds are formed. The configurational assignments of (V) at C_{13} and C_7 are based on the steric requirements. The C-20 methyl group is in close contact with $C_{12'}$ methylene group on the case of forming C_7–$C_{13'}$ and C_{13}–$C_{7'}$ bonds on the β-side in the dimer, since predominance of α-attack on the C-ring of resin acids[18] is known.

The irradiation of palustric acid (VII) in n-hexane without a sensitizer under nitrogen reached photoequilibrium between palustric acid (VII) and the ring-opened triene (VIII) as DAUBEN, et al. has reported[12], and with acetophenone or benzophenone, palustric acid (VII) was dehydrogenated dehydroabietic acid (VI).

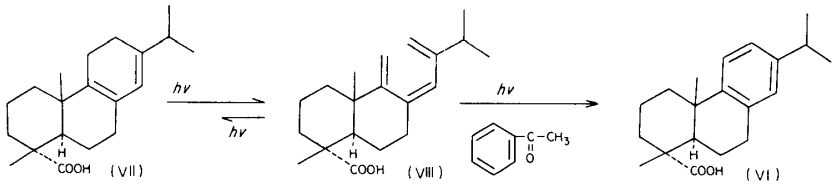

Fig. 3.

Photochemical excitation and the subsequent reactions of levopimaric acid would seem to involve the excited singlet state in the absence of a sensitizer[11], and to involve the excited triplet and singlet states in the presence of a sensitizer. The dimerization of levopimaric acid could seem to occur by a concerted mechanism in the excited tri-

plet state of which lifetime is longer than that of the excited singlet state as follows.

$$S \xrightarrow{h\nu} {}^1S^* \longrightarrow {}^3S^*, \quad {}^3S^* + L \longrightarrow {}^3L^* + S, \quad {}^3L^* + {}^3L^* + L\text{-}L$$

S, $^1S^*$ and $^3S^*$ represent respectively the ground state, the excited singlet state and the excited triplet state of a sensitizer (acetophenone, benzophenone). L and $^3L^*$ represent the ground state and the excited triplet state of levopimaric acid.

Since the distance between C-7 and C-13 in either the excited singlet state or the excited triplet state of abietic acid is too large, the excited π orbitals can not overlap at C-7 and C-13, and the ring-opening reaction like the photoreaction of palustric acid is impossible because of the heteroannular diene system, the cycloaddition reaction of two abieic acids might proceed by a concerted mechanism in the singlet or triplet excited state.

$$S \xrightarrow{h\nu} {}^1S^* \longrightarrow {}^3S^*, \quad {}^3S^* + A \longrightarrow {}^3A^* + S, \quad A \xrightarrow{h\nu} {}^1A^*, \quad {}^1A^* \text{ or } {}^3A^* \longrightarrow A\text{-}A$$

A, $^1A^*$ and $^3A^*$ represent the ground state, the excited state and the excited triplet state of abietic acid.

The mechanism of the dimerization is consistent with spin conservation rule and Woodward-Hoffman rule.

It seems that palustric acid either in the excited singlet state or in the excited triplet state prefers a half-chair comformation which leads to ring opening but not a half-boat comformation which leads to bond formation[11]. The dimerization of palustric acid in the half-chair conformation could not seem to occur on spacial ground. Therefore it seems that the irradiation of palustric acid (VII) without a sensitizer reaches photoequilibrium between palustric acid and the ring-opened triene, and with acetophenone dehydroabietic acid (VI) is yielded by the hydrogen-abstraction from palustric acid by acetophenone in the photoequilibrium.

half chair　　half boat

Further experimental data will be needed for complete elucidation of the results obtained in the present experiment.

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